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Quantitative differentiation of coal, char and soil organic matter in an Australian coal minesoil

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1. Highlights

- Measuring soil organic matter in coal minesoil complicated by coal and char.
- Coupled thermal-chemometric method distinguished and quantified organic C pools.
- Provision of initial estimates for end-member components improved MCR model fits.
- Geogenic C represented < 20% of total organic C in tested minesoils.
- Estimated proportions of SOM were consistent with Walkley-Black measurements.

Abstract

Organic inputs from plant establishment are part of the rehabilitation process in restoring coal minesoil function. Soil organic matter (SOM) content could therefore potentially be an indicator of rehabilitation success. Rehabilitated coal minesoils contain inherited coal and char that complicate the attribution of measured total C to recent SOM inputs. We provide proof-of-principle tests of ramped combustion thermal analyses combined with chemometrics (multivariate curve resolution - alternate least squares, MCR-ALS) to quantitatively distinguish between geogenic C, pyrogenic C and SOM C in model mixtures and a coal minesoil from Queensland, Australia. MCR-ALS successfully separated coal and char, and initial estimate

thermograms improved the model fits. Geogenic C represented a small proportion of total organic C in the tested unknown minesoils (mean = 9.2%), and a larger contribution from pyrogenic C (mean = 32.4%). Trends in SOM were also consistent with Walkley-Black measurements of organic C. Our combined thermal-chemometric approach represents a robust means of quantifying SOM, distinct from coal and char, though resolution could be improved using multi-element thermograms and additional end-members and soils.

Keywords

minesoil; soil organic matter; geogenic carbon; pyrogenic carbon; thermal analysis; multivariate curve resolution

2. Introduction

Minesoils are the soils created during the rehabilitation of mined lands, typically covering the newly constructed landforms [1, 2]. The landforms created with the overburden must be stabilized and rehabilitated before relinquishment. In particular, opencut mining of coal moves large quantities of overburden and soil. In 2014, ~230 Mt of coal was produced from opencut mines in Queensland, Australia [3] and $\sim 1.5 \times 10^9$ bank cubic meters of overburden was moved [4]. Rehabilitated mined lands usually use stockpiled topsoil to spread over spoil and overburden materials, often in a layer no thicker than 0.3 m. Mixing of these different materials, topsoils and spoils, during their reapplication is common. These soils are therefore developmentally young, with little to no organic matter due to losses during stockpiling, disturbance and dilution from mixing with overburden material [1, 5].

Incorporation of soil organic matter (SOM) from plant and microbial detritus during plant establishment are part of the rehabilitation process in restoring soil quality and function [6]. Beyond reclamation, direct and indirect measures of SOM content are frequently used in assessments of agricultural soil quality and health [7, 8]. Improved soil quality can reduce erodibility and stabilize these landforms, thus fulfilling rehabilitation objectives. Soil organic matter (SOM) derived from the accumulation of recent plant and microbial inputs could therefore potentially be used as an indicator of rehabilitation success. In addition, disturbed minesoils also represent an opportunity to act as an important sink for atmospheric CO₂ as SOM levels increase [9, 10], though they likely do not represent a net sequestration of C since they are part of the fossil fuel production process.

The artificial nature of landform construction on a mine site is reflected in a highly uneven distribution of carbon across a mine site creating a high spatial heterogeneity of carbon originating from various sources [11]. Minesoils at coal mines contain variable amounts of inherited coal particles from waste rock removed during mining, and coal dust from aeolian deposition. Coal dust accumulation from nearby operations may also continue after initial reclamation. This complicates the quantification of soil carbon from recent SOM inputs attributable to rehabilitation. The quantification of SOM accumulation in Australian coal minesoils is further complicated by the potential presence of pyrogenic C derived from the incomplete combustion of biomass from wildfires. This char, or black carbon (BC), has been investigated for its potential to remain in the soil for centuries [12]. Pyrogenic C is found commonly in soils globally [13-15] and is nearly ubiquitous in Australian soils and especially in Vertisols [13, 16]. Vertisols and Solonchaks are the predominant soil types in the coal mining region of interest to this study – the Bowen Basin, Queensland, Australia [17]. Quantifying SOM carbon accumulated in mined lands during rehabilitation therefore requires distinguishing this carbon from that which is inherited from the starting materials used for reclamation.

Ussiri et al. [2] provide a comprehensive overview of the methods for quantifying geogenic C (*i.e.*, coal) in rehabilitated minesoils, which they classify as: optical/microscopic, thermal, chemical, spectroscopic, molecular markers, isotopic, or some combination of these. The most reliable method to quantify geogenic C is radiocarbon analysis, owing to lack of radiocarbon activity due to age, but the analysis is prohibitively expensive for routine use, particularly in cases requiring large sample numbers such as carbon stock assessment in rehabilitated land. ^{13}C -NMR spectroscopy has also been used [18], but frequently requires sample pre-treatments and long run times thus also making it time-consuming, expensive, and impractical for high sample numbers. In response, infrared spectroscopy (FTIR, DRIFT) combined with multivariate data analysis (partial least squares (PLS)) was proposed as a more rapid and practical approach [19], but the PLS statistical approach requires large calibration data sets that might be soil-specific or only locally applicable, which represent an expensive and time consuming set of reference measurements. Similarly, methods to quantify pyrogenic char in soils generally involve elemental analysis after removal of more labile organic matter either by chemical or thermal oxidation [20, 21], or direct detection by pyrolysis-GC/MS, ^{13}C -NMR or thermogravimetry [22]. More recently, Rock-Eval analysis uses ramped pyrolysis and combustion to discern different types of organic materials in soil and sediment samples [23-25], and has been compared to conventional methods for distinguishing BC from SOM [26-28].

As geogenic C, pyrogenic C and soil organic matter C combust at different temperatures, the application of ramped combustion to distinguish among them is an attractive approach. However, each of these components is actually composed of a spectrum of materials that

combust over a range of temperatures, making the distinction with a single temperature cut-off challenging. The interpretation of thermograms as the primary result from ramped combustion of carbon-containing substrates may be carried out qualitatively or (semi-)quantitatively. Multivariate curve resolution - alternate least squares (MCR-ALS) is defined as a group of statistical techniques that help resolve mixtures by determining the number of constituents, their response profiles (*e.g.*, spectra) and their estimated concentrations, using a minimal number of assumptions about the nature and composition of these mixtures [29-31]. MCR-ALS has been successfully applied to a variety of biological and chemical processes with near infrared (NIR) spectroscopy [32, 33], FTIR spectroscopy [34, 35] and discrete data such as concentrations of different pollutants [36]. However, to our knowledge, this technique has not been applied to resolve thermal analysis curves or to the characterization of organic matter in surface soils.

The objectives of this study were to first provide a proof-of-principle test of whether thermal analyses combined with the MCR-ALS chemometric technique are able to distinguish between and quantify proportions of geogenic C, pyrogenic C and soil organic matter C in model mixtures of increasing complexity. A series of experimental mixtures combining various mineral matrix and organic C end-members were subjected to CO₂ evolved gas analysis (CO₂-EGA) during ramped combustion (*i.e.*, thermal analysis). MCR-ALS analyses were applied to the resulting thermograms to generate modeled estimates of the different forms of organic C. A second objective was to test the approach against a set of minesoils of unknown composition to generate estimates of the proportional contributions of geogenic C (coal), pyrogenic (or black) C (BC) and soil organic matter C (SOC) to the total organic C content. The ultimate goal is to provide a robust method for quantifying soil organic matter C accumulations during the rehabilitation of minesoils.

3. Materials and Methods

2.1. Reference materials and mixture end-members

2.1.1. Geogenic carbon

Bituminous coal from the BHP Billiton Mitsubishi Alliance Goonyella coal mine (21°45'32"S 147°58'37"E) and from the Anglo American German Creek coal mine (22°54'35"S 148°33'57"E) were selected as the reference materials for geogenic C. As these coal samples originated from mines within the Bowen Basin, they were assumed to be similar to coal particles found in rehabilitated minesoils in the vicinity of the mined resource. The coal samples

were collected in July and August 2010 as grab samples from stockpiles. The samples were oven dried at 40 °C, and homogenized by ball milling.

2.1.2. Pyrogenic carbon

Chestnut (*Castanea sativa*) wood char was used as reference material to represent pyrogenic, biomass-derived BC. The char was produced by pyrolysis at 450 °C for 5 hours, and has been used in the international BC ring trial [20, 37]. Wood char was selected because the historical vegetation cover at the research sites was dominated by Brigalow (*Acacia harpophylla*) scrub, a woody plant that is regularly subjected to fire [38].

2.1.3. Carbon-free mineral matrix

Laboratory grade, acid washed sand was re-washed with 4 M HCl solution and heat treated in a muffle furnace at 600°C for 48 hours to remove all organic C, including BC. Sand was ball milled to improve homogeneity of mixtures. While the quartz mineralogy is not necessarily representative of the mineralogy of the regional soils, it is useful as a simplified model mineral matrix.

2.1.4. Coal-free, BC-containing soil matrix

A sandy clay (37% clay) Vertisol soil sample collected from Urrbrae, South Australia [21], previously used in the international BC ring trial [20], was selected as a reference material to represent a natural matrix containing SOM and pyrogenic BC, without containing geogenic coal. The soil was previously found to contain 3-30% of its organic C as pyrogenic BC (depending on the method used), with the remainder as SOM [21]. This soil was selected because Vertisols, as well as other high clay containing soils, are common in the Bowen Basin [17].

2.1.5. Minesoil matrix

Rehabilitated minesoils were collected from the BMA Blackwater coal mine (23°28'0"S 148°46'0"E) in the Bowen Basin in Queensland, Australia, as a reference minesoil matrix for experimental mixtures because of its low organic and inorganic carbon concentrations. The area is in the Brigalow Belt bioregion, which is semi-arid with periods of both intense rainfall and long dryness [39]. Vegetation at the site is dominated by buffel grass (*Cenchrus ciliaris*). Minesoil samples were collected from 0.1-0.2 m depth. The soils were oven dried at 40°C, sieved to pass a 2.0-mm mesh, ground to pass a 0.5-mm mesh for Walkley-Black [40] organic C and elemental analyses, and ball milled for improved homogeneity prior to thermal analysis.

2.2. Experimental mixtures

A total of 31 experimental mixtures containing Goonyella coal and BC, individually and combined, were created with three different mineral matrices: sand, Vertisol and Blackwater minesoil (Table 1, Table A1). All mixtures, with the exception of the sand+BC, were made with ball milled materials and homogenized in a vial by end-over-end shaking for 30 minutes. The sand+BC mixtures underwent elemental analysis shaken, but unground, and were manually ground with mortar and pestle prior to thermal analysis.

Three sand+BC mixtures were made to target 1%, 2% and 3% weight proportions of BC. The true weight proportions of the mixtures were 1.007%, 2.451%, 3.205% of BC by weight. Using a reported C concentration of 682.0 g C kg⁻¹ for the BC [37], the resulting estimated C concentrations of the mixtures were 6.87 g C kg⁻¹, 16.7 g C kg⁻¹ and 21.9 g C kg⁻¹. These simple mixtures were not subsequently used in the MCR analyses, but used along with the mixtures of Vertisol+BC (see below) to test the efficacy of combustion-based elemental analyses in quantifying pyrogenic C.

Nine different sand+BC+coal mixtures were made to generate target C concentrations of 0.5%, 1% and 2%, using the reported C concentrations of 682.0 g C kg⁻¹ for BC [37] and a measured C concentration of 655.6 g C kg⁻¹ for the Goonyella coal (see below). For each target C concentration, the concentration was achieved by adding BC and Goonyella coal in 1:1, 1:2 and 2:1 mass ratios. The mixtures were made by weighing out the sand, adding the coal, reweighing the partial mixture, then calculating how much BC to add to generate the desired target C concentrations.

Six different Vertisol+BC mixtures were designed to target 0.5%, 1%, 1.5%, 2% 2.5% and 3% weight proportions of BC. Actual weight proportions were 0.510%, 0.995%, 1.466%, 2.086%, 2.556% and 3.097%. Using the reported C concentrations of 26.7 g C kg⁻¹ for the Vertisol [21] and 682.0 g C kg⁻¹ for the BC [37], the estimated total C concentrations of the mixtures were thus 30.04 g C kg⁻¹, 33.22 g C kg⁻¹, 36.31 g C kg⁻¹, 40.37 g C kg⁻¹, 43.45 g C kg⁻¹ and 46.99 g C kg⁻¹, where the proportions of mixture C attributable to the added BC ranged from 11.6% to 44.9%. It is important to remember that the C contained in the Vertisol itself was a combination of BC and soil organic matter, as noted in Section 2.1.4.

Three Vertisol+coal mixtures were designed for target coal proportions of 1%, 5% and 11% by weight of Goonyella coal. Actual weight proportions were 0.996%, 5.323% and 11.189%. Using the reported C concentrations of 26.7 g C kg⁻¹ for the Vertisol [21] and a measured C concentration of 655.6 g C kg⁻¹ for the Goonyella coal, the resulting estimated C concentrations of the mixtures were 6.53 g C kg⁻¹, 34.9 g C kg⁻¹ and 73.4 g C kg⁻¹. The added coal represented 19.8% to 75.6% of the mixture C.

One Vertisol+BC+coal mixture was made using an aliquot of the Vertisol+0.5%BC mixture described above and adding Goonyella coal to achieve a target proportion of 0.5% coal by weight. The actual mixture was 0.510% BC by weight and 0.549% coal by weight. The resulting estimated C concentration of the mixture was 25.27 g C kg⁻¹, of which 21.1% of the mixture total C was attributable to the added BC and coal.

Nine different minesoil+BC+coal mixtures were made to generate target C concentrations of 2%, 3% and 4%, using the reported C concentrations of 682.0 g C kg⁻¹ for BC [37], and measured C concentrations of 655.6 g C kg⁻¹ for the Goonyella coal and a measured C concentration of 11.9 g C kg⁻¹ for the Blackwater minesoil (see below). For each target C concentration, the concentration was achieved by adding BC and coal in 1:1, 1:2 and 2:1 mass ratios. The mixtures were made by weighing out the minesoil, adding the coal, reweighing the partial mixture, then calculating how much BC to add to generate the desired target C concentrations. The proportions of total mixture C attributable to the added BC ranged from 13.2% to 49.7%, and the added coal represented 13.5% to 48.3% of the mixture C.

2.3. Reclaimed minesoils of unknown composition

The efficacy of the analytical and statistical approaches developed using the experimental mixtures of known compositions was tested on a series of minesoil samples of unknown composition. A soil profile (0-0.3 m) was dug using spades and trowels at a 26-year-old rehabilitation site at the Capcoal AngloAmerican German Creek coal mine. Sampling was performed at several depth increments (0-0.5, 0.5-1, 1-2, 2-5, 5-10, 10-20, and 20-30 cm) using a trowel and tape measure.

2.4. Analytical techniques

2.4.1. Elemental analyses

Literature values were used for the carbon concentrations of the BC and Vertisol, while C concentrations of the Goonyella and German Creek coals, sand and minesoils were measured. Multiple techniques for the quantification of C in these samples were used because of the highly recalcitrant nature of the pyrogenic and geogenic C expected to be present in the samples. Total and organic C in the coal samples were determined by Rock-Eval 6 [41]. Since Rock-Eval is used routinely in the petroleum industry, it was decided that this analysis would provide better accuracy than regular elemental analysis [41, 42], which may combust samples at too low a temperature for complete C recovery. Total C concentrations of the sand and minesoils were determined by dry combustion using a LECO TruSpec CHN autoanalyser. For comparison, organic C concentrations of the minesoil samples were also determined using the Walkley-Black [40] method, which we expected to generate substantially smaller C concentrations than the

combustion-based methods, but were more closely representative of SOM exclusive of pyrogenic and geogenic C [27].

2.4.2. Analytical thermal analysis

Thermal analyses (*i.e.*, simultaneous thermogravimetry, differential scanning calorimetry, evolved-gas analysis) were performed to characterize the thermal stability of the different end-member reference materials and experimental mixtures, with the expectation that thermal stability of the various forms of C could be used to distinguish among them. German Creek minesoil samples were subsequently subjected to thermal analysis as the true unknown samples to test the method. Analyses were performed according to Fernández et al. [43] using a Netzsch STA 409PC Luxx equipped with a type-S (Pt/PtRh) TG-DSC sample carrier supporting a PtRh10-Pt thermocouple (Netzsch-Gerätebau GmbH, Selb, Germany). Evolved gas analysis (EGA) during ramped combustion was performed using a LI-840 CO₂/H₂O infrared gas analyzer (IRGA, LI-COR Biosciences, Lincoln NE, USA) coupled to the outlet of the STA instrument. Samples were weighed into 85- μ L Pt crucibles with pierced lids to a mass of approximately 30 mg for soils and mixtures, and 2-4 mg for BC and coal. Samples were heated from 30 to 800 °C at 10 K min⁻¹, with an isothermal pause at 105 °C to eliminate sample moisture, under a flowing atmosphere of CO₂-free Ultra-Zero air. Resulting CO₂-EGA thermograms are expressed in units of ppm_v of CO₂ per mg of sample. Prior to MCR analysis (see below), the thermograms were normalized by the area under the CO₂-EGA curves (*i.e.*, by the total CO₂ detected by the IRGA).

2.5. Statistical analyses

We applied multivariate curve resolution - alternate least squares (MCR-ALS) techniques to CO₂-EGA thermograms as an empirical, quasi-quantitative means of determining the concentrations of SOM, BC and coal in the experimental mixtures as proof-of-principle, then applied the technique to a set of minesoils of unknown composition. MCR-ALS is a multivariate deconvolution technique allowing the separation of one or several end-members (also called pure components), which in our case corresponded to CO₂-EGA thermograms of coal, BC and SOM, from unresolved mixtures when no prior information is available about the nature and composition of these mixtures [29]. When available, providing initial guesses for the pure components helps the algorithm converge to finding pure components as close as possible to the prescribed ones. We performed MCR-ALS analyses with and without initial guesses to determine the robustness of the resulting models. When initial guesses were used, the CO₂-EGA thermograms of BC, coal, or Vertisol and Blackwater minesoil without additional BC or coal were provided as the pure components to be separated by the MCR-ALS. In the case of the unknown minesoils, initial guesses of the SOC pure components were not possible because they were the desired results, but pure German Creek coal and BC were included in the analytical set.

We performed the MCR-ALS analyses using The Unscrambler® software v10.1 (Camo Software AS, Oslo, Norway). Four MCR analyses were performed during the proof-of-principle phase, each with and without initial guesses of pure components provided. The first MCR was performed to separate BC and coal from a simple matrix not containing organic C using the sand+BC+coal mixtures ($n = 9$), with BC and Goonyella coal provided as pure components when initial guesses were used. When initial guesses were not provided, the BC and coal thermograms were included as samples in the analytical set. The second MCR was performed to separate SOC and BC using the Vertisol+BC mixtures ($n = 6$), with Vertisol and BC provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The third MCR was performed to separate SOC, BC and coal using the Vertisol+coal mixtures ($n=3$), Vertisol+BC mixtures ($n = 6$) and the Vertisol+BC+coal mixture ($n = 1$) for a total of 10 samples, with Vertisol, BC and coal provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The fourth MCR was performed to evaluate the separation of SOC, BC and coal in a minesoil with a different SOC composition than the Vertisol, using the Blackwater minesoil+BC+coal mixtures ($n = 9$), with Blackwater minesoil, BC and coal provided as pure components when initial guesses were used, or included in the analytical set when initial guesses were not used. The outputs of the MCR-ALS analyses are modeled thermograms of the constituent components resolved from the experimental mixture thermograms (*i.e.*, SOC, BC and coal) and the areas under these curves, which are then expressed as relative concentrations in the initial unresolved mixture [44].

MCR-predicted C proportions of total organic C were calculated as the modeled area assigned to a specific component (*e.g.*, BC) divided by the total area modeled for all components combined, and expressed as a percentage. The relationships between the MCR-predicted C proportions and the calculated C concentrations of the various mixtures, based on the proportions of added BC and coal, were evaluated using least-squares linear regression. The ability of the regression models to explain the variance in the data was assessed using the coefficient of determination (R^2). Ideal MCR-predicted versus calculated C values would follow the 1:1 line with no significant deviations (*i.e.*, non-zero intercept and/or slope different from 1). Deviation of the MCR-predicted values from the 1:1 line was assessed using root mean square error (RMSE), which is expressed in % of total organic C.

4. Results

3.1. Organic C concentrations of reference materials, experimental mixtures and unknown minesoils

Elemental analysis of the sand confirmed minimal contamination (Table 2), and thermal analysis did not detect any evidence of thermally stable C indicative of pyrogenic or geogenic C (data not shown). Organic C concentrations in the Blackwater minesoil used in the experimental mixtures was relatively low (11.9 g C kg⁻¹, Table 2). Its composition was dominated by SOM as indicated by the fact that Walkley-Black organic C represented 94% of the total. The high C concentrations in coal samples exceeded the reliably determinable levels of the LECO analyzer, which produced unusually low results (data not shown). Rock-Eval analysis found that the Goonyella and German Creek coals differed in C concentration (Table 2), but ramped combustion by thermal analysis data showed that the CO₂-EGA thermograms of the two coals were similar, thereby justifying the use of the more C-rich Goonyella coal in the experimental mixtures as a substitute for the German Creek coal. Similar to coal, the BC material was known to have high concentrations of recalcitrant C that may result in low yields from the LECO analyzer. Evidence for this was provided by correlation analysis of estimated versus LECO-measured C concentrations in the Sand+BC and Vertisol+BC mixtures (data not shown). Values were highly correlated ($R^2 = 0.988$), but biased (slope = 0.845) and thus indicated that measured values underestimated the true values. The proportions of Walkley-Black organic C to total C in the German Creek minesoil samples ranged from 67% to 84% (Table 2), indicating substantial contributions from recalcitrant components. As a result, the measured total C concentrations of these samples should be considered underestimates. It is therefore difficult to attribute confidence to absolute concentrations of the various components determined by the MCR-ALS method, and therefore we report only relative proportions.

3.2. MCR analysis for the separation of BC from coal in unresolved sand mixtures

Thermograms of BC and coal reference materials were relatively simple, with a single dominant peak at 531 °C for BC (Fig. 1a) and at 545 °C for coal (Fig. 1b). The major distinctions between the two thermograms were a more pronounced shoulder at around 400 °C for the coal, and greater thermal stability for coal than for BC, as indicated by a higher peak temperature and higher end temperature of the exotherm, which exceeded 600 °C for the coal. These thermograms were used as pure component initial guesses, and the small differences are exploited in the MCR analysis to partition the carbon sources despite the relative similarity of the CO₂-EGA thermograms.

When no pure component initial guesses were provided, the MCR-ALS analysis was able to distinguish the BC and coal in sand+BC+coal mixtures (Fig. 2a). However, while the MCR-

generated thermogram of BC was similar to the actual, this was less so for the coal thermograms (Fig. A1b). As might be expected, when initial guesses were provided the MCR-generated thermograms were much more similar to actual thermograms (Fig. 2b and A2), with maximum peak temperatures of 529 °C for component 1 (corresponding to BC) and a maximum peak temperature of 545 °C for component 2 (corresponding to coal).

The regression between calculated and MCR-predicted proportions of total carbon corresponding to BC and coal showed a good performance of the MCR model, with an R^2 of 0.97 and RMSE of 22.9 % of total C, though the slopes were substantially different from the 1:1 line (Fig. 2c, Table 3). When the thermograms of BC and coal were used as initial guesses of the pure components, RMSE decreased to 18.4% of total C (Fig. 2d) and slopes were closer to the 1:1 line (Table 3). Deviations of the regression lines from the 1:1 line (deviation of the slope from 1 and deviation of the intercept from 0) indicated the necessity to correct the MCR-predicted values using the linear regression equation before the MCR model could be used in practice.

3.3. MCR analysis for the separation of BC from SOC in unresolved Vertisol mixtures

The Vertisol SOM had a more complex thermogram compared to BC and coal, with a major peak at 450 °C and smaller peaks and shoulders at 350 °C, 380 °C and 525 °C (Fig. 1c). Additions of BC to Vertisol resulted in the largest increases in the thermogram peak near 525 °C, but also smaller increases in other smaller peaks (Fig. 3). Increases in smaller, low temperature peaks were generated by the low temperature tail of the BC thermogram (Fig 1a).

MCR was able to clearly distinguish between SOC and BC in the Vertisol mixtures, whether or not initial guesses for pure components were provided (Fig. 4). MCR-generated thermograms were similar to actual thermograms, as would be expected when pure components are identified (Fig. A2). When pure components were not provided, the MCR-generated thermograms remained similar, but a larger portion of the CO₂ emissions from 500-600 °C were attributed to the BC than the SOM components (Fig. A1).

Slopes of the regressions between calculated and MCR-predicted proportions of total carbon corresponding to BC were similar both with and without provided pure components, but the intercepts changed substantially (Table 3). When the pure component initial guesses were provided, MCR underestimated the amount of added BC, and RMSE increased slightly (Fig. 4d). This is possibly attributable to the fact that the Vertisol also contains some BC, which is not accounted for in the analysis.

3.4. MCR analysis for the separation of BC and coal from SOC in unresolved Vertisol mixtures

With increased complexity of adding coal to the Vertisol+BC mixture, MCR was still able to generate distinct end-members whether or not pure component initial guesses were provided (Fig. 5a and 5b). However, the provision of initial guesses substantially improved the

similarity between MCR-generated and actual thermograms, particularly for the coal component (Fig. A1 and A2).

Provision of the initial guesses also substantially improved MCR-generated estimates of the proportions of coal, BC and SOC (Fig. 5c and 5d). Without the initial guesses, no relationship was found between calculated and MCR-generated proportions of BC, while the correlation was much stronger ($R^2=0.97$) when initial guesses were provided. The initial guesses also reduced RMSE values for BC, coal and SOC. Slopes of the regressions were also substantially closer to 1 and intercepts were substantially closer to 0 when initial guesses were provided (Table A2).

3.5. MCR analysis for the separation of BC and coal from SOC in unresolved minesoil mixtures

The thermogram the Blackwater minesoil consisted of a single broad peak near 370 °C (Fig. 1d). Consistent with the Walkley-Black organic C results (Table 2), the thermogram showed little contribution of thermally recalcitrant C. The Blackwater minesoil thermogram contrasts substantially with the more complex Vertisol thermogram, which may reflect the relatively short developmental age and lack of organic inputs in the minesoil.

MCR was able to distinguish between coal, BC and SOC in the minesoil mixtures with or without initial guesses despite the coal and BC samples having similar peak combustion temperatures and a large overlap (Fig. 6a and 6b). The provision of initial guesses substantially improved the similarity of MCR-predicted and actual thermograms, particularly for the coal end-member (Fig. A1 and A2). MCR estimates for SOC were improved by the initial guesses, decreasing RMSE from 18.2% to 4.4% of TOC (Fig. 6c and 6d), though the parameters of the regressions were not substantially changed (Table A2). Estimates for BC and coal were reversed when initial guesses were provided, such that BC was overestimated without initial guesses but underestimated with initial guesses. These observations were reversed for coal. Under optimal conditions (when guesses were provided), the correlation of BC was the weakest ($R^2 = 0.43$) among the components, likely due to its intermediary nature in terms of recalcitrance and similarity to coal.

3.6. MCR analysis for the quantitative distinction of coal, BC and SOC in minesoil samples

MCR analysis of the thermograms of the German Creek minesoil samples did not include initial guesses, but thermograms of German Creek coal and the chestnut wood char BC were included in the analysis. MCR-generated BC and coal thermograms were similar to those generated in previous MCR analyses without initial guesses provided (Fig. 7a compared to Fig. 5a and 6a). The MCR-generated thermogram for BC was reasonably similar to its actual thermogram, while the thermograms for German Creek coal differed substantially (Fig. A1). The MCR-generated thermogram for SOC (Fig. 7a, solid), which has no known/actual analog was more similar to that of the Vertisol than the Blackwater minesoil in that it had two main peaks.

The second, smaller peak could be thermally stable (*i.e.*, strongly mineral-adsorbed) soil organic matter, a form of BC or coal that is dissimilar to the identified pure components, or inorganic (carbonate) C. The SOC thermogram also has a prominent shoulder near 350 °C, which might indicate the presence of a distinct pool of easily oxidized/combusted SOM. MCR-estimated partitioning of the total C of the German Creek minesoils resulted in the largest proportion contributed by SOC, followed by BC, and the smallest contribution by coal (Fig. 7b). C contributions from BC and coal also appeared to decrease with soil depth, though this trend was not statistically significant.

5. Discussion

The most common methods for differentiating recent (*i.e.*, SOM) and geogenic C pools involve chemical, thermal or combined methods to remove SOM followed by subsequent analysis of the residue. Chemical methods for SOM removal include hydrogen peroxide (H₂O₂), sodium hypochlorite (NaOCl), disodium persulfate (Na₂S₂O₈), among others [2], and rely on the fact the geogenic C is resistant to chemical oxidation due to its highly condensed aromatic chemical structure. Another approach similar to the chemometric approach proposed in the current study is the determination of lignite C by ¹⁴C analysis coupled with fast prediction by DRIFT spectroscopy and PLS regression [19]. However, this approach excludes the separation of recently charred materials (BC) having similar ¹⁴C signature as recent SOM and requires the collection of large datasets of costly laboratory reference measurements to calibrate the PLS regression models.

Thermal oxidation methods rely on the fact that geogenic C is typically more thermal resistant than SOM owing to diagenetic processes, and temperatures between 300 and 400 °C are typically used as a cut-off [21, 45-47]. The challenge with these methods is that a single chemical or temperature cut-off between recent and geogenic C does not account for the wide spectrum of properties of each of these components. That is, in some cases highly recalcitrant SOM is not adequately oxidized or conversely some portion of coal is oxidized, leading to over- or underestimation of one pool or the other. Adding to the complications is the frequent presence of pyrogenic C (*i.e.*, recent, fire-derived BC). The quantification of BC in soils and sediments varies greatly between methods [20], largely due to a wide continuum of BC properties attributable largely to the properties of the fire that produced it. BC frequently represents an intermediary form of organic matter between SOM and coal in terms of recalcitrance and thermal stability, and many of the methods outlined above are unable to distinguish between BC and coal [47].

Deconvolution of EGA-CO₂ thermograms using MCR-ALS can directly apportion different components of the soil C pool, and avoids the interference of water mass loss experienced using

thermogravimetry as well as the problems associated with empirical cut-off temperatures. In this study, the MCR results show a distinct separation of the coal and char but overestimated the coal contribution (Fig. 2b and 6b) in some cases. This bias towards the material with a higher temperature of combustion may be due to some interference by the mineral matrix if it protects BC materials, thus increasing the combustion temperature [48-50], or due to differing thermal stability of the BC and coal components in the unknown soils compared to the reference materials used. The provision of initial estimate thermograms for end-member components improved the MCR model fits as expressed by smaller RMSE, calculated MCR-estimated regression slopes closer to 1, and regression intercepts closer to zero. The one exception to this was that RMSE for the regression for coal content increased from 12.0 to 20.3 when initial guesses were provided for the Blackwater minesoil+BC+coal experimental mixtures (Fig. 6c versus 6d). It is unclear what produced this anomaly because the MCR-predicted thermograms for coal were substantially more similar to the measured thermogram when initial guesses were used (Fig. S1b versus S2b). While BC and coal were well differentiated in these samples, other high-temperature chars and anthracite coals may pose more substantial challenges to thermal differentiation because of possible overlap. For the purposes of minesoil reclamation, the differentiation of BC is important as it would be considered more recent C than coal and might be included as arising from rehabilitation if fires are known to have occurred post-reclamation. These challenges might be overcome through the use of several end-member initial guesses in the MCR analyses from a variety of char and coal materials with varying thermal stability, the use of multi-element thermal analysis [51], or through the coupling of CO₂-EGA with radiocarbon analysis [e.g., 52, 53] where coal might be differentiated on the basis of the radiocarbon concentration of the CO₂ evolved at various temperatures of combustion – particularly in the potentially overlapping region. While this coupled approach is compelling, the cost of multiple radiocarbon analyses per sample would likely make the approach prohibitive in many applications. The presence of carbonates and other inorganic carbon sources may also pose a problem in the broader application of the method. Carbonates frequently decompose at temperatures similar to the combustion temperatures of pyrogenic and geogenic organic C. This poses a potential problem in distinguishing these pools, such that greater total carbon concentrations attributable to carbonates could inflate the MCR estimates for pyrogenic and geogenic C, and therefore be less reliable. Sample pre-treatment with acid to remove carbonates or addition of carbonate end-member thermograms (which were not performed in the current study) may alleviate this problem.

Thermal analysis results indicated that geogenic C represented a small proportion of the total organic C in the unknown minesoils of this study (*e.g.*, up to 21%, with mean = 9.2%), and a larger contribution from pyrogenic C (*e.g.*, up to 41%, with mean = 32.4%). However, the issue

of under-estimating total organic C concentrations is problematic, and prevents the absolute quantification of the various components. Even Rock-Eval analysis, which has been well correlated to elemental analysis, has been shown to under-estimate total organic C in soils [28].

Trends in the estimated proportions of SOM based on thermal analysis and MCR-ALS were consistent with proportions of Walkley-Black [40] measurements of organic C (Table 2), though the correlation was not especially strong ($p = 0.17$, $R^2=0.35$; data not shown). Walkley-Black values were greater than the thermal analysis-derived values for SOM, which is not surprising as the Walkley-Black procedure is known to oxidize a varying portion of BC, depending on particle size, C concentration and the degree of thermal alteration of the BC, making it possible to overestimate SOM in recently rehabilitated minesoils with low total organic C [27, 54, 55]. Walkley-Black also significantly underestimates C in many organic substrates and is influenced by soil texture and soil depth [55, 56]. As such, while Walkley-Black might serve to give an indication of plant-derived, new organic carbon accumulation and has been used for this purpose in coal-containing sediments [27], there is a long history of recommending against the method for the purposes of distinguishing between SOM carbon stocks and pyrogenic and geogenic forms of C [57].

6. Conclusion

Thermal analysis using ramped combustion has been used for the quantification of BC in sediments and soils [22, 58] and in quantification of coal in mine soils [59]. However, a single cut-off temperature to distinguish between components during ramped combustion can be problematic, and thermogravimetry can overestimate because some mass loss during ramped combustion is not associated with organic matter oxidation. Through a series of experiments, we demonstrated that materials with similar thermal properties (*i.e.*, char and coal) can be distinguished and proportionally quantified in natural soils as well as in minesoils using ramped combustion measuring CO₂-EGA paired with chemometric analysis using MCR-ALS. While the inclusion of known end-members in the MCR-ALS analysis improved the estimates, our results suggest that the approach may be appropriate when no such initial guesses are available. The unknown minesoils tested appeared to have relatively low geogenic C concentrations. It is unclear whether MCR estimates would be more or less robust if there were greater proportions of geogenic and pyrogenic C, and further testing with other soil types, is needed to extend the applicability of this technique to other soils. The development of a set of initial end-member guesses beyond the single BC and coal reference materials used in the current study is also required to deal with likely variability in thermal stability of different char and coal type found in coal minesoils.

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Figure captions

Figure 1. CO₂ evolved gas analysis (CO₂-EGA) thermograms of reference end-members used in experimental mixtures: (a) pyrogenic carbon in the form of chestnut wood char black carbon (BC), (b) geogenic Goonyella coal C, (c) Vertisol and (d) Blackwater minesoil.

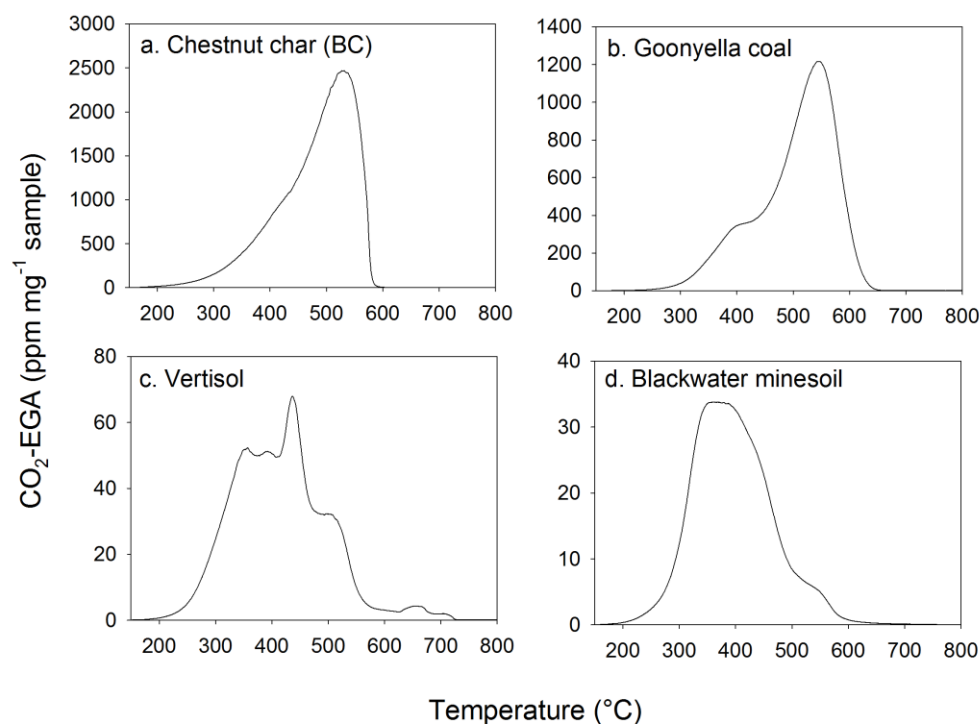


Figure 2. MCR analysis for the separation of black carbon (BC) and coal from sand+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC and coal contents without (c) and with (d) initial guesses provided. Clusters of three data points having similar proportions of calculated C are not replicates, but mixtures made with differing ratios of BC and coal (*i.e.*, 1:1, 1:2, 2:1). Because of the mixed-ratio mixtures, total C is determined by summing the largest values of coal to the smallest values of BC for the 2:1 and 1:2 mixtures, and summing the middle values for the 1:1 mixtures. Relative intensity refers to proportion of total CO₂ evolved (ppm per total ppm).

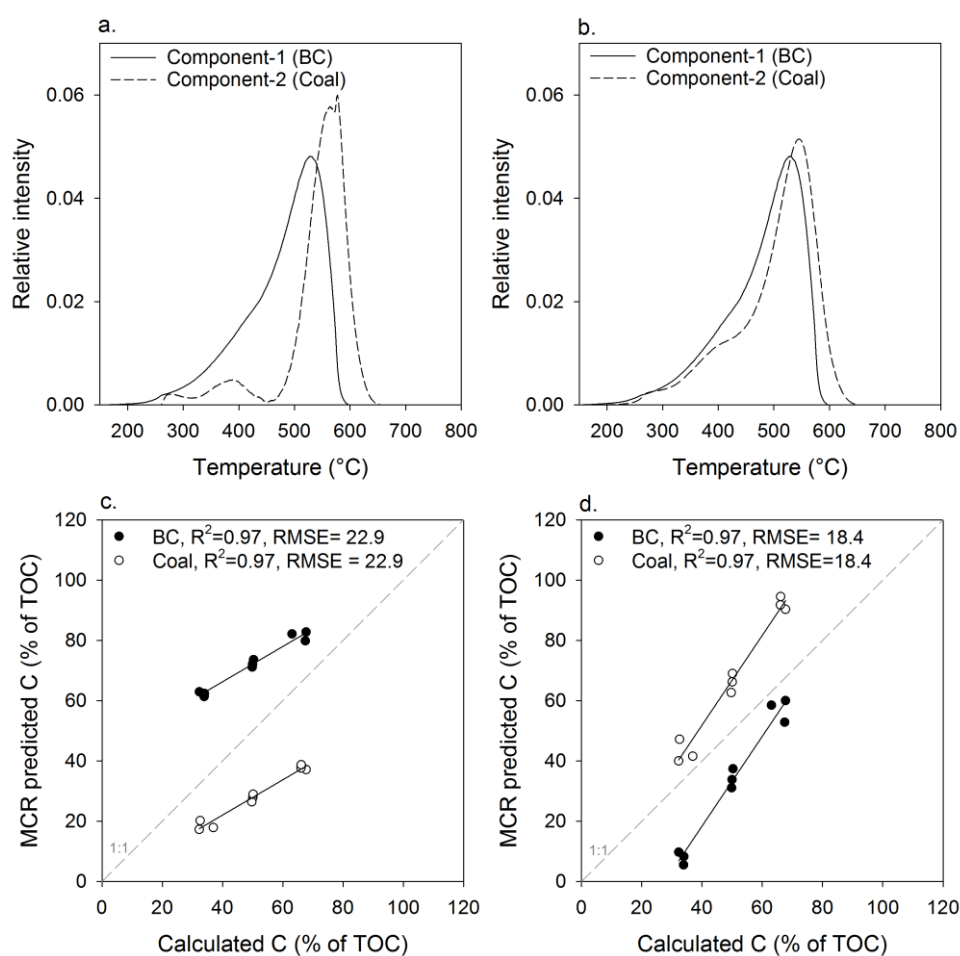


Figure 3. CO₂ evolved gas analysis (CO₂-EGA) thermograms of experimental mixtures composed of a Vertisol with different amounts of chestnut wood char black carbon (BC) added.

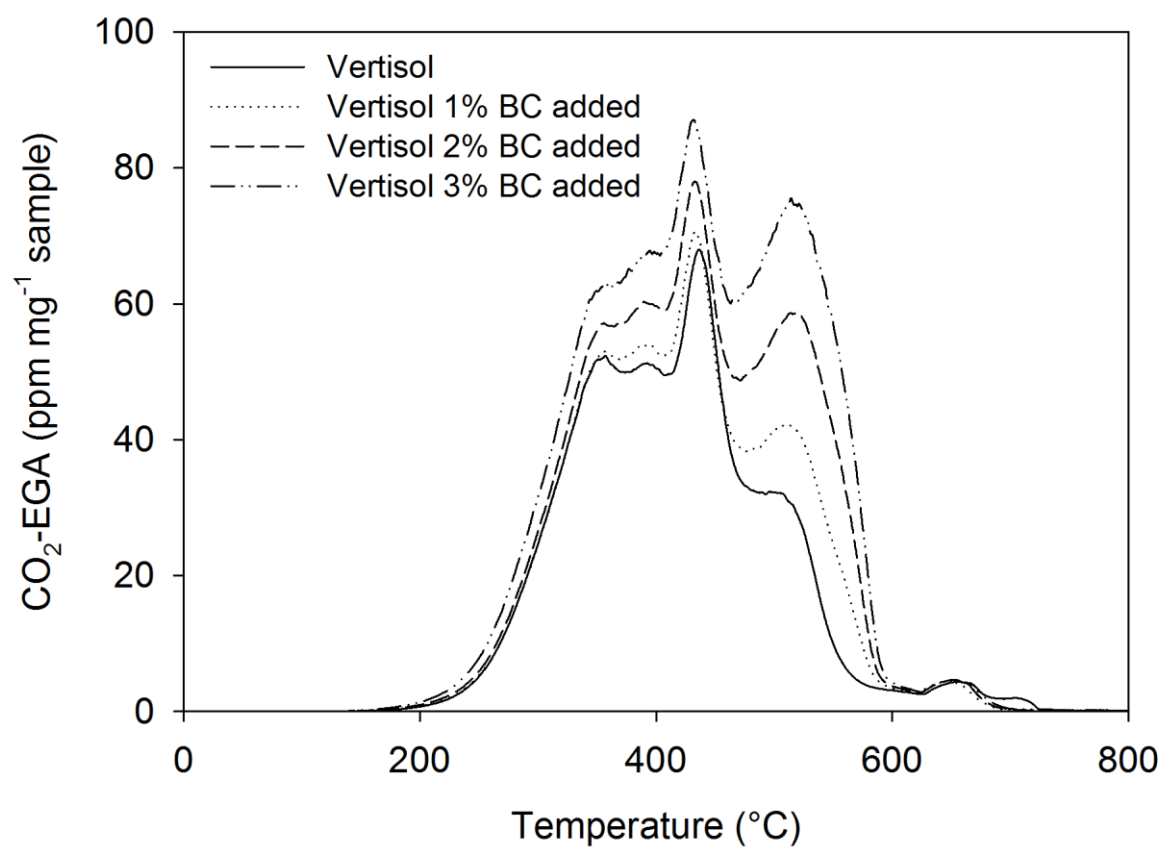


Figure 4. MCR analysis for the separation of soil organic carbon (SOC) and black carbon (BC) from Vertisol+BC experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC content without (c) and with (d) initial guesses provided. Relative intensity refers to proportion of total CO₂ evolved (ppm per total ppm).

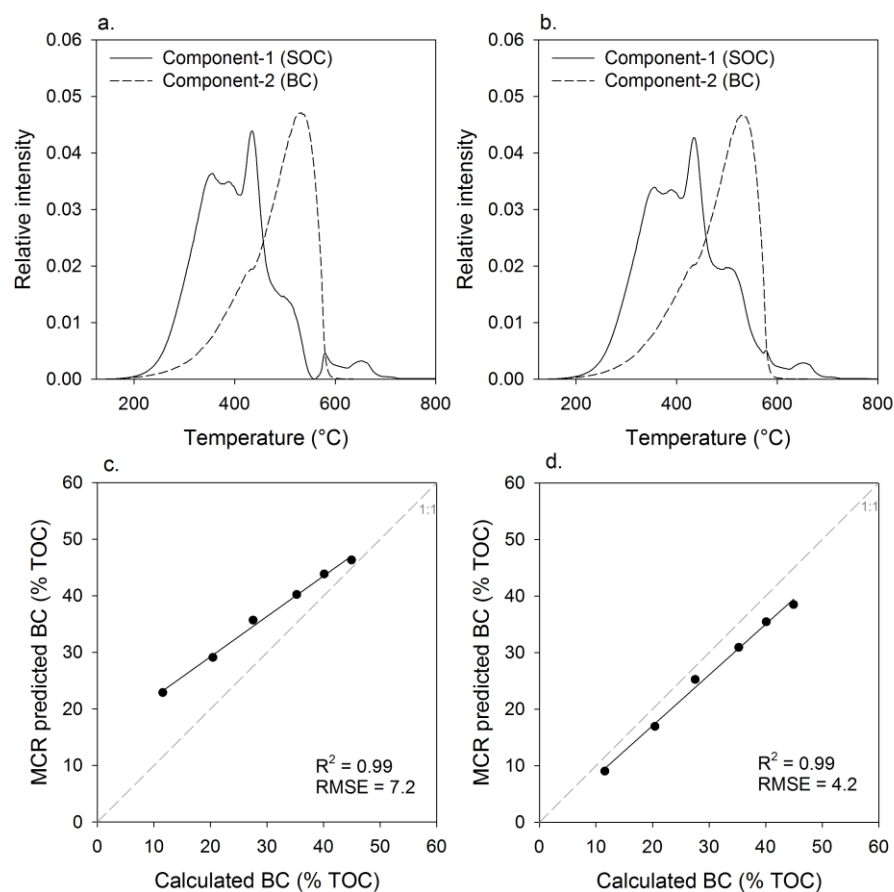


Figure 5. MCR analysis for the separation of soil organic carbon (SOC), black carbon (BC) and coal from Vertisol+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC, coal and SOC contents without (c) and with (d) initial guesses provided. Relative intensity refers to proportion of total CO₂ evolved (ppm per total ppm).

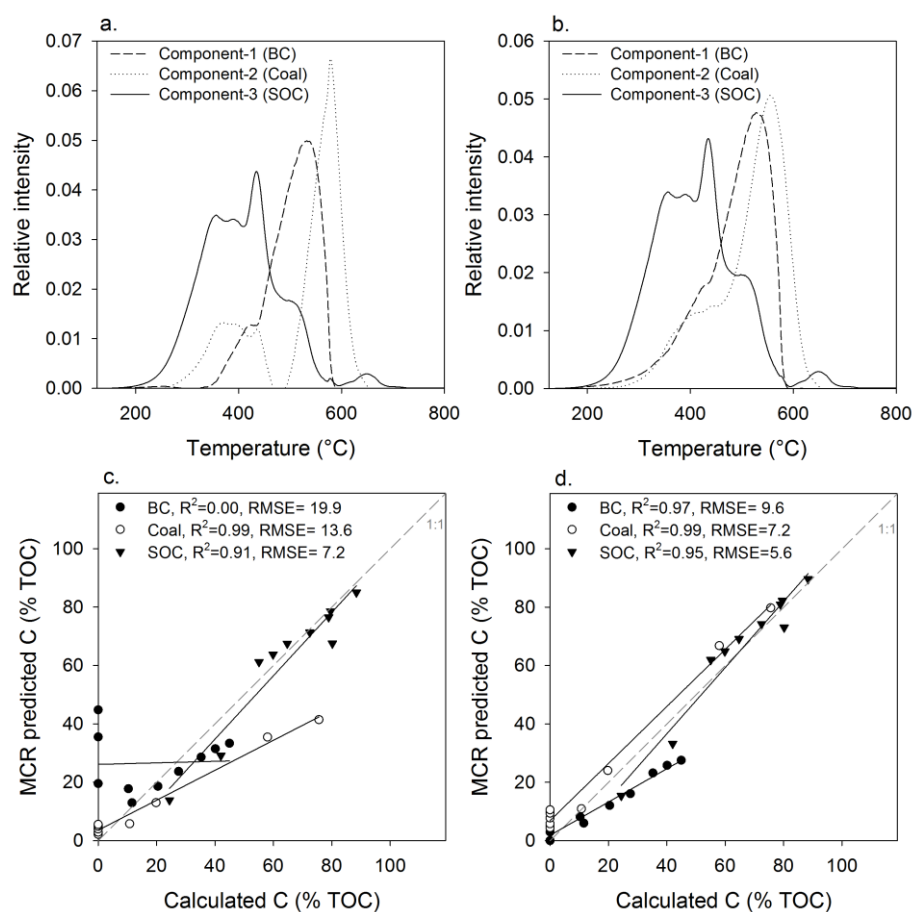


Figure 6. MCR analysis for the separation of soil organic carbon (SOC), black carbon (BC) and coal from Blackwater minesoil+BC+coal experimental mixtures. Thermograms of the pure components separated by MCR without (a) and with (b) initial guesses provided, and MCR predicted BC, coal and SOC contents without (c) and with (d) initial guesses provided. Relative intensity refers to proportion of total CO₂ evolved (ppm per total ppm).

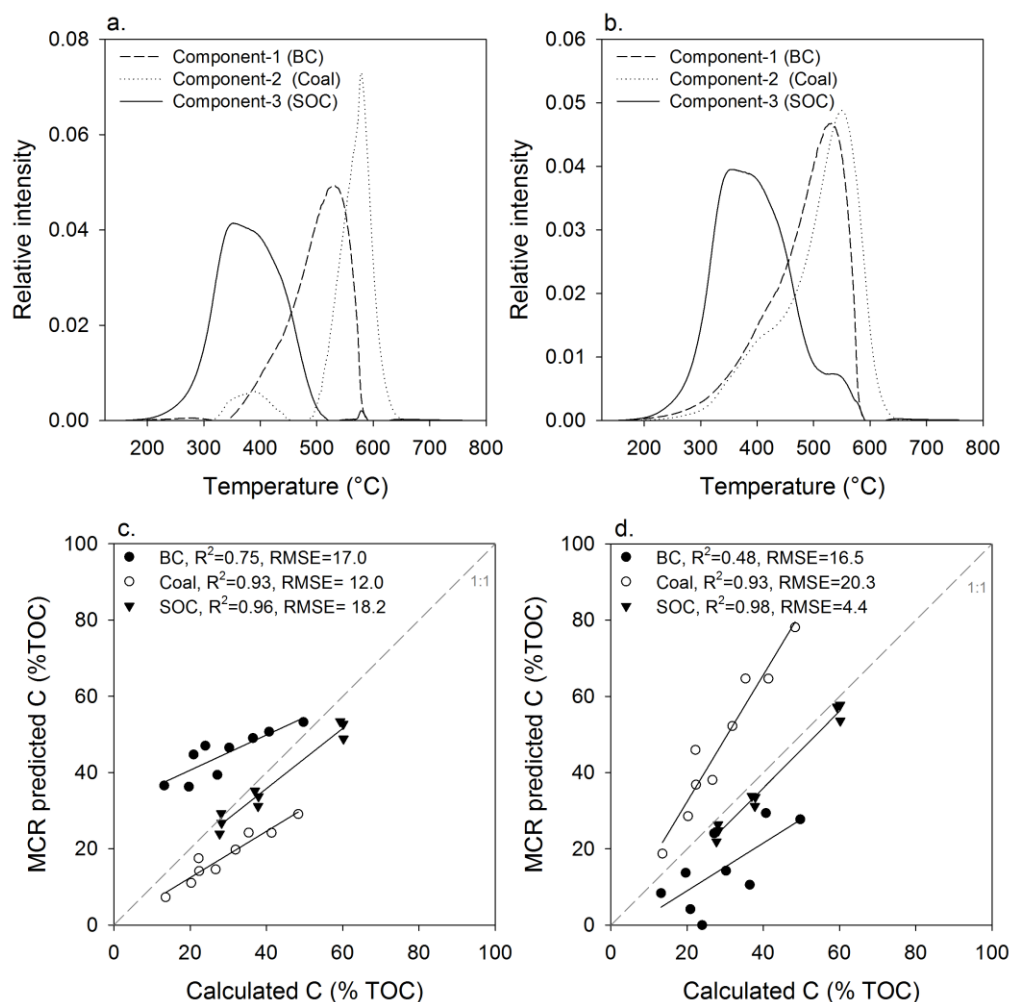


Figure 7. MCR analysis for the separation of black carbon (BC), coal and soil organic carbon (SOC) from a depth profile of a minesoil of unknown composition. Thermograms of the pure components separated by MCR (a) and MCR predicted BC, coal and SOC contents (b). Relative intensity refers to proportion of total CO₂ evolved (ppm per total ppm).

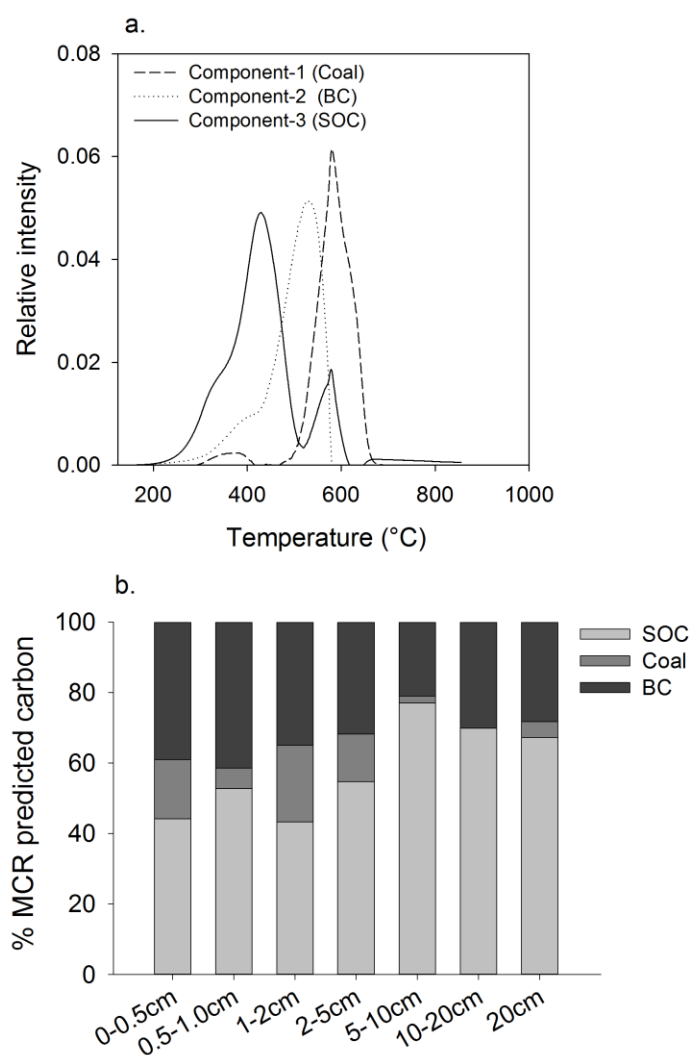


Table 1. Experimental mixtures generated of pyrogenic C (chestnut char, BC) and geogenic C (Goonyella coal) mixed with three mineral matrices used in proof-of-principle thermal analyses

Matrix	BC	Goonyella Coal	BC+Coal
Sand	1%, 2%, 3% by weight		0.5%C 1:1, 1:2, 2:1
			1%C 1:1, 1:2, 2:1
			2%C 1:1, 1:2, 2:1
Vertisol	0.5%, 1%, 1.5%, 2%, 2.5%, 3% by weight	1%, 5%, 11% by weight	0.5% + 0.5% by weight
Blackwater minesoil			2%C 1:1, 1:2, 2:1
			3%C 1:1, 1:2, 2:1
			4%C 1:1, 1:2, 2:1

Table 2. Measured carbon concentrations of end-member materials used in mixtures and mine soils. Total C concentration of the coals were determined using Rock-Eval, while dry combustion elemental analysis was used for the sand and mine soils. Values of “nd” indicate that sample was not analyzed using the particular method.

Sample	Total C (g C kg ⁻¹ soil)	Walkley-Black organic C (g C kg ⁻¹ soil)
Sand	0.06 ±0.04 (n=2)	nd
Goonyella coal	656	nd
German Creek coal	604	nd
Blackwater mine soil (10-20cm)	11.9	11.2
German Creek mine soil (0-0.5 cm)	18.0	11.9
German Creek mine soil (0.5-1 cm)	16.4	11.0
German Creek mine soil (1-2 cm)	19.8	13.3
German Creek mine soil (2-5 cm)	20.4	13.9
German Creek mine soil (5-10 cm)	10.0	8.4
German Creek mine soil (10-20 cm)	19.0	12.0
German Creek mine soil (20-30 cm)	12.0	8.6

Table 3. Regression equations between calculated carbon distributions in the black carbon (BC), coal and soil organic carbon (SOC) fractions (x) and the carbon distribution in the fractions predicted by MCR-ALS (y) based on the regressions presented in Figs. 2b, 4b, 5b, 6b.

Mixture	Initial Guesses	BC	Coal	SOC
Sand + BC + Coal	with	$y = 1.49 x - 41.24$	$y = 1.49 x - 7.72$	
	without	$y = 0.59 x + 42.84$	$y = 0.59 x - 1.39$	
Vertisol + BC	with	$y = 0.90 x - 0.88$		
	without	$y = 0.71 x + 14.94$		
Vertisol + BC + Coal	with	$y = 0.57 x + 1.81$	$y = 0.98 x + 6.85$	$y = 1.13 x - 8.77$
	without	$y = 0.03 x + 26.09$	$y = 0.51 x + 3.55$	$y = 1.09 x - 8.66$
Minesoil + BC + Coal	with	$y = 0.63 x - 3.53$	$y = 1.66 x - 0.86$	$y = 1.01 x - 4.24$
	without	$y = 0.46 x + 31.39$	$y = 0.61 x + 0.29$	$Y = 0.79 x + 4.27$